SIMULATION OF METHYLDIETHANOLAMINE-CARBON DIOXIDE-WATER SYSTEM USING EQUILIBRIUM APPROACH

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CERTIFICATE

This is to certify that the thesis entitled, "**SIMULATION OF METHYLDIETHANOLAMINE- CARBON DIOXIDE -WATER SYSTEM USING EQUILIBRIUM APPROACH"**, submitted by Mr. Vishal Mohanty, Roll no. 110CH0394, in partial fulfillment of the requirements for the award of degree of Bachelor of Technology in Chemical Engineering at National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

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ABSTRACT

As the climate is changing very frequently and global warming is increasing at an alarming rate, there is a need to mitigate greenhouse gases which have gained a top most priority. As the main source of CO_2 emission is fossil fuels (mainly in power plants), there is a need to keep check on utilization of fossil fuels. Carbon capture and sequestration (CCS) is one of the methods which enable the utilization of fossil fuels with lower CO_2 emissions. Commercially CO_2 capture by chemical absorption is very active. While number of solvents for CO_2 absorption by chemical method has been proposed, comparison on performance of different solvents has not been done properly and claims on different solvent vary widely. The work done here emphasize on absorption of CO_2 by the solvent and then stripping the solvent to obtain pure CO_2.This thesis has been prepared to evaluate the performance of solvent – methyldiethanolamine(MDEA) on CO_2 absorption.

In this thesis, comprehensive flow sheet model has been built for the solvent system, using ASPEN Plus as the modeling tool. The Thermodynamic model using ENRTL model for CO_2 capture has been done and effect of reboiler duty, solvent flow rate and so on has been observed.

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NOMENCLATURE

r	:	Rate of a reaction
k_2	:	Second-order rate constant
R	:	Universal gas constant
T	:	Temperature
Kj	:	Equilibrium constant for the reaction j
$\Delta Gj°(T)$	:	Gibbs free energy change for reaction j at temperature T
s	:	Solvent
$G_s(T)$	:	Solvent *s* Gibbs free energy at temperature T
$G_s^{ig}(T)$	:	Solvent s ideal gas Gibbs free energy at temperature T
$\Delta G_s^{igfl}(T)$	:	Departure of Gibbs free energy from ideal gas to liquid at temperature T
ΔH_{abs}	:	Heat of absorption/mole of CO_2
H^l_{final}	:	Final solution's molar enthalpy
$H^l_{initial}$	:	Initial solution's molar enthalpy
H^g_{CO2}	:	Gaseous CO_2 absorbed molar enthalpy
n_{final}	:	Total number of moles in the final solution
$n_{initial}$	:	Total number of moles in the initial solution
¥	:	Activity coefficient of species i in solution
n_i	:	Number of moles of i
G^E	:	Excess Gibbs free energy
P	:	Pressure
G^{id}	:	Excess Gibbs free energy if the mixture were ideal
L	:	Total molar flow of liquid
G	:	Total molar flow of gas

CHAPTER-1

INTRODUCTION

1.1 CARBON CAPTURE AND SEQUESTRATION

As the climate change fear has achieved a great importance, various methods have been developed to mitigate CO_2 emission. For the last 5 decades there has been growing concern as the average global temperature is increasing at a moderate rate. Figure 1-1 tells us about the rise in the difference between the global mean surface temperature and the average temperature from 1961-1990 [1].

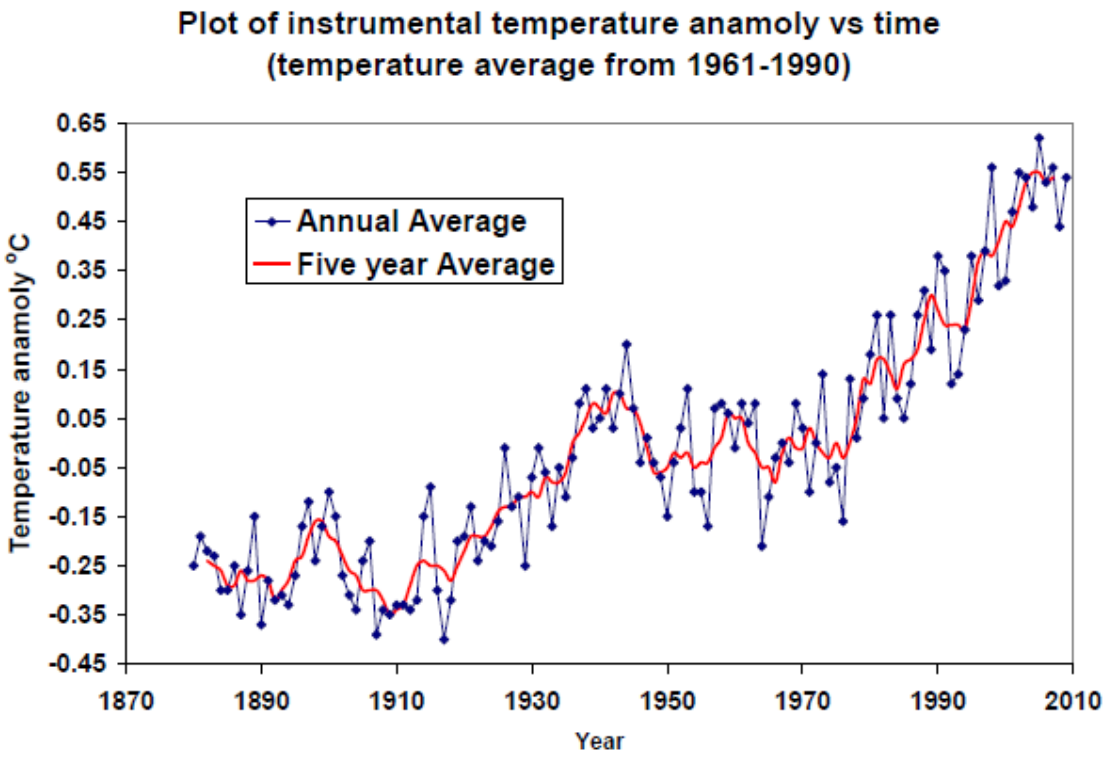

Figure 1-1: Plot of global instrumental temperature anomaly vs. time (temperature average from 1961-1990) [1].

The main cause behind increase in CO_2 is due to various activities adopted by human beings which directly or indirectly contribute to the rise in CO_2 concentration.

From figure 1-2 it can be seen that CO_2 concentration is increasing at a concerned rate. So there is need to mitigate CO_2 emissions.

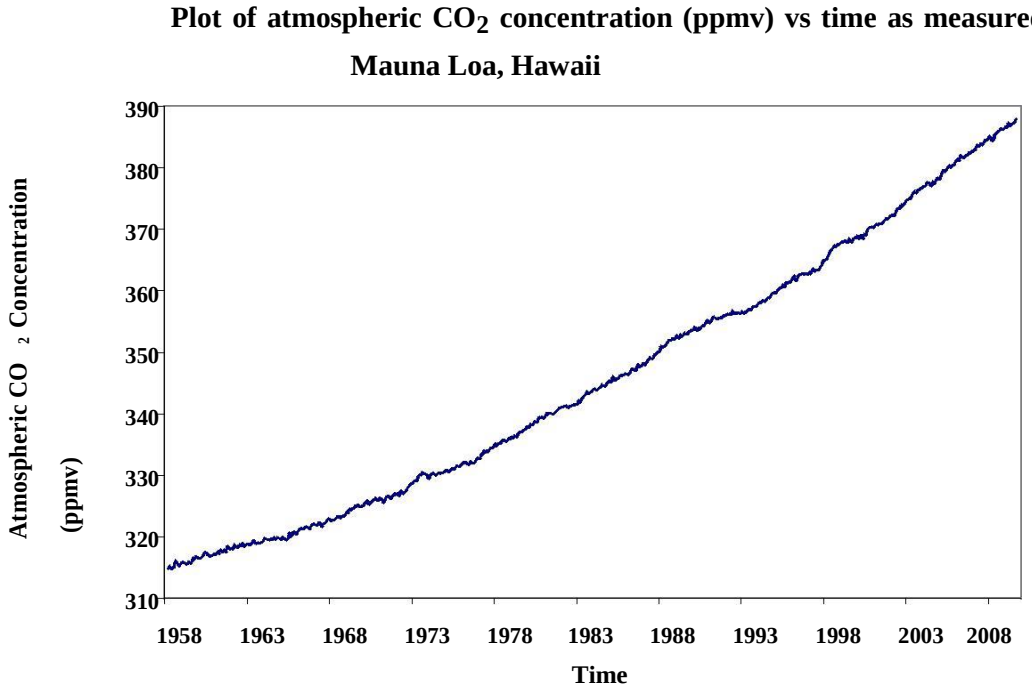

Figure 1-2: Plot of atmospheric CO_2 concentration (ppmv) vs. time as measured at Mauna Loa, Hawaii [2].

The main source for the increase in CO_2 concentration in the atmosphere is electricity generation sector which mainly comprises of Natural gas and Coal fired power plants. So there is a urgent need of deploying CO_2 mitigation technologies on this sector which will provide a cleaner environment in future.

1.2 BRIEF OVERVIEW OF CO_2 CAPTURE SYSTEMS

Three processes for CO_2 capture have been classified which are as follows:-

i)Post-Combustion Capture
ii)Oxyfuel Combustion
iii)Pre-Combustion Capture

1.2.1 POST-COMBUSTION CAPTURE

In this process, CO_2 is removed from the flue gas produced after combustion of the fuel. A schematic of post-combustion capture is presented in Figure 1-3

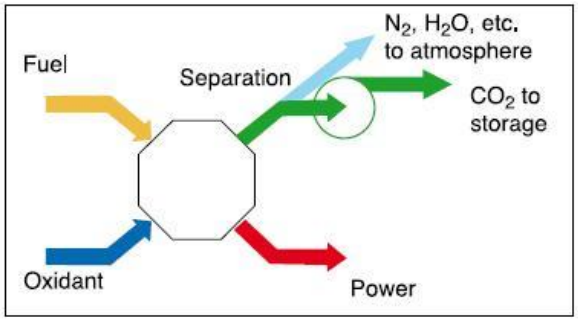

Figure 1-3: Mechanism of post-combustion capture [3]

Various post-combustion methods are Chemical absorption, Physical absorptions, Membrane separation, Adsorption, Cryogenic separation.

1.2.1.1 CHEMICAL ABSORPTION

CO_2 is removed from the flue gas by passing the gas through the continuous scrubbing system. Usually, an absorber and a desorber together make the scrubbing system. In the absorber, reversible reaction between CO_2 and solvent (amine) takes place. In the desorber, the CO_2 which was absorbed by the solvent (amine) is stripped off and a pure stream of CO_2 is produced, which is then sent for compression and the regenerated solvent is sent back to the absorber.

1.2.1.2 PHYSICAL ABSORPTION

Physical absorption which is also known as non-reactive absorption takes place between two phases, either the gas is absorbed by the liquid, or the liquid is absorbed by a solid.

When the gas is absorbed by the solvent in the liquid phase, some amount of gas moves into the liquid. For example, oxygen may be absorbed by the water. At the liquid gas interface the mass transfer is taken place and the rate is dependent both upon the gas and the liquid. The absorption is dependent on gas solubility, the pressure and the temperature. When the liquid is absorbed by a solid, some amount of liquid moves into the solid. For example, water may be absorbed by the pot (clay) in which it is stored. At the liquid solid interface the mass transfer is taken place and the rate is dependent both on the liquid and the solid.

1.2.1.3 MEMBRANE SEPARATION

The process by which materials are selectively separated through pores or minute gaps in the molecular arrangement of a continuous structure is known as Membrane separation. Membrane separations are classified on the basis pore size as well as the separation driving force.

Table 1-1: CO_2 partial pressure in flue gases of different combustion systems. [3]

Flue gas source	CO_2 concentration, % vol (dry)	Pressure of gas stream, MPa	CO_2 partial pressure, MPa
Natural gas fired Boilers	7-10	0.1	0.007-0.01
Gas turbines	3-4	0.1	0.003-0.004
Oil fired boilers	11-13	0.1	0.011-0.013
Coal fired boilers	12-14	0.1	0.012-0.014
IGCC after combustion	12-14	0.1	0.012-0.014
IGCC synthesis gas after gasification	8-20	2-7	0.16-1.4 (before shift)

1.2.2 OXYFUEL COMBUSTION

Here instead of air, combustion is taken place in the presence of oxygen which prevents dilution of CO_2 with other gases.

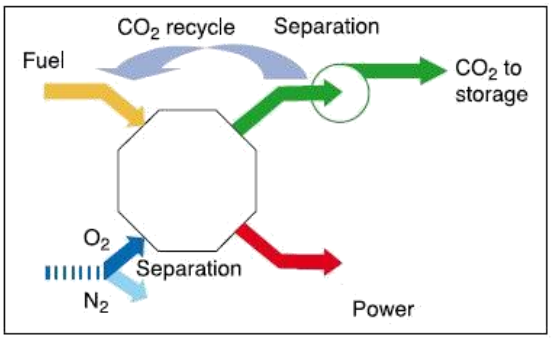

Figure 1-4: Mechanism of oxyfuel combustion [3]

1.2.3 PRE-COMBUSTION CAPTURE

In this process, carbon content of the fuel is reduced before combustion so as to produce pure CO_2 on combustion. Figure 1-5 presents a schematic of precombustion decarbonization.

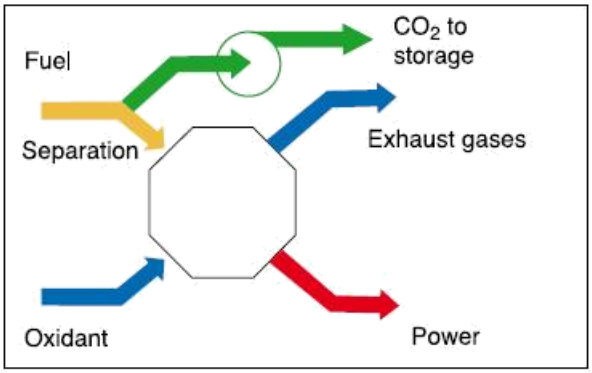

Figure 1-5: Mechanism of precombustion decarbonization [3]

1.3 THESIS OBJECTIVE

The main objective of the thesis is to develop an energy efficient absorption and capture of CO_2 using methyldiethanolamine (MDEA).

1.4 SCOPE OF THE THESIS

The scopes of this thesis are as follows:

1. To develop a thermodynamic model which can describe thermodynamic and thermal properties of CO_2-H_2O-alkanolamine system over different pressure, temperature and amine concentration range

2. To determine the parameters which affect the performance of the CO_2-H_2O-alkanolamine system

3. To optimize the different dependent parameters to get the best results and maximum CO_2 capture percentage

1.5 OUTLINE OF THE THESIS

The work is divided into 7 chapters. Chapter 1 of this thesis tells about the carbon capture and sequestration and various process involved with it and about the thesis objectives. Chapter 2 involves the studies of the previous work that has been done on the given topic and discussion about the amines involved and the reaction mechanism. Chapter 3 describes about the methyldiethanolamine system. This chapter also tells about the actual process going on and the

model used to describe the system. Chapter 4 shows the developed thermodynamic model for CO_2-H_2O-MDEA and tells about the various parameters (inputs) used for modeling the system. Chapter 5 describes the result and discussion for this work. It tells about the effect of various parameters on the system. Chapter 6 presents overall conclusions from this thesis. Chapter 7 discusses further direction in which this study can be carried forth.

CHAPTER-2

LITERATURE REVIEW

By reviewing work from previous studies, it provides a motivation and direction for this work. Additionally, some of the results will be comparable to the results seen later in this work.

Upon surveying it was found that more than 60 years ago in chemical industries (mostly oil industries, power plant) Amine scrubbing technology for removal of H_2S and CO_2 from various gas streams was adopted. This technology commercially is the most widely used process for capturing CO_2.

2.1 AMINE PROCESS

In most of the industries absorption with the help of chemical solvents, which is also known as chemical absorption is the commercially most widely used process to remove acid gas(mainly CO_2 and H_2S) from various gas streams. Currently preferred chemical solvents for acid gas removal by chemical absorption are amine based absorbents.
Alkanolamines, which are the combinations of alcohols and ammonia, are the mostly preferred solvents for removing acid gas. In addition to natural gas processing, chemical absorption of acid gases by alkanolamines has been utilized in a various industries like petroleum refining, CO_2 capture from combustion and flue gases, removal of CO_2 from synthesis gas in ammonia or hydrogen plants.

2.2 AMINE TYPE

Though there are many amines available but commercially 4 types of amines are used which are primary amines (e.g. MEA), secondary amines (e.g. DEA), tertiary amines (e.g. MDEA) and cyclic amines (e.g. PZ) [4].

As there are three alkyl groups present in MDEA, the reaction between CO_2 and MDEA is hindered. Therefore, CO_2 dissolves in H_2O first to form carbonic acid (H_2CO_3), and then carbonic acid reacts with amine. The following reaction takes place

$$CO_2 + H_2O + MDEA \leftrightarrow MDEAH^+ + HCO_3^- \quad \text{-- (2.1)}$$

For determining the solubility of CO_2 in MDEA as well as in other Alkanolamines, the ENRTL (electrolyte NRTL) [5-7] was used by Posey [8] and Austgen et al. [9]. For determining the VLE data for the MDEA- H_2O-CO_2 system, The Pitzer's equation [10] was used by Kuranov et al. [11] Kamps et al. [12] and Ermatchkov et al. [13]. For determining the Solution Enthalpy of CO_2 in aq. MDEA, the data for VLE were combined with the Pitzer's equation by Arcis et al. [14]

and the thermodynamic model was applied. For analyzing the VLE for absorption of CO_2 in aq. MDEA, The extended UNIQUAC model [15] was used by Faramarzi et al. [16]. Concentration of MDEA solutions containing CO_2 was also predicted and was compared to the concentration measured by NMR spectroscopy [17, 18].

Nowadays aqueous solutions of MEA are used mainly. The major advantages of MEA are: large reactivity, cheap, and less capacity for absorption of hydrocarbons. The main disadvantages of MEA are: High corrosiveness of MEA which increases by temperature, large heat of reaction with CO_2 and H_2S results in large energy requirements for the regeneration of solvent and subsequently the total cost for the process is raised, relatively large vapor pressure which sees amine losses through vaporization [4].

Though MDEA is costlier than MEA, but it has lower rate of reaction with CO_2 as compared to other amines which makes it suitable to use in various industries.

The main reactions taking place in CO_2-MDEA-H_2O system are as follows [4]:

Water dissociation equilibrium:

$$2H_2O \leftrightarrow H_3O^+ + OH^- \quad \text{-- (2.2)}$$

Bicarbonate formation equilibrium:

$$CO_2 + 2H_2O \leftrightarrow H_3O^+ + HCO_3^- \quad \text{-- (2.3)}$$

Carbonate formation equilibrium:

$$H_2O + HCO_3^- \leftrightarrow H_3O^+ + CO_3^{2-} \quad \text{-- (2.4)}$$

MDEA protonation equilibrium:

$$H_3O^+ + MDEA \leftrightarrow H_2O + MDEA^+ \quad \text{-- (2.5)}$$

2.3 REACTION MECHANISM

The rate equation for the reaction of tertiary amines (MDEA) with CO_2 is given by the equation [19]

$$r=k_2[MDEA][CO_2] \quad \text{-- (2.6)}$$

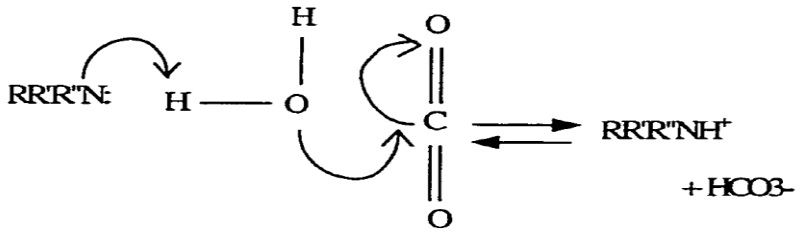

Figure 2-1: Reaction of tertiary amines with CO_2

Direct reaction of CO_2 with amine is not possible. Therefore, water must be present so that the reaction takes place by above mechanism [19].

Barth et al. proposed two other mechanisms for the reaction of amines with CO_2 in addition to simple second order mechanism. The first is the zwitterion mechanism, in which there is a possibility of forming an intermediate [19].

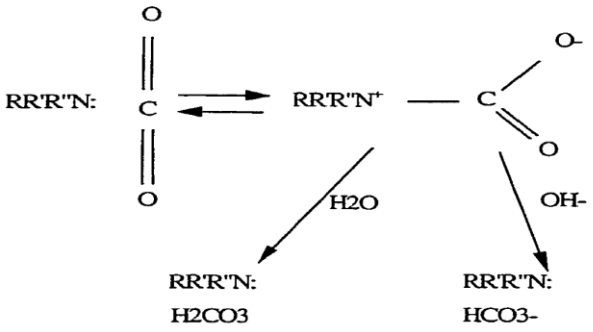

Figure 2-2: Zwitterion mechanism

The second mechanism is the formation of alkyl carbonates which has got a rare chance to occur in solutions with high pH.

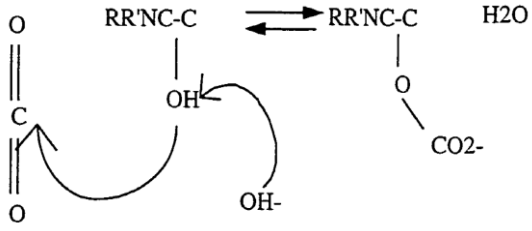

Figure 2-3: Alkyl carbonates formation mechansim

The reason that MDEA acts well is that it does not react with CO_2 appreciably. Therefore, it absorbs this gas very slowly. Certain additives like piperazine are used so as to increase the rate

of reaction between CO_2 with MDEA. By adding required amount of additives to MDEA, desired amount of CO_2 can be removed.

Posey analyzed that Absorption of CO_2 into the aqueous MDEA solutions is controlled by mass transfer mechanism with chemical reaction. Therefore, Solubility is required for calculating the mass transfer driving force. Thus for predicting equilibrium solubility at desired conditions of temperature, MDEA concentration and CO_2 loading, a thermodynamic equilibrium is highly demanded. Bishnoi also suggested that for calculating free amine concentration, thermodynamics is also needed. To determine the quantity of free amine for a specified overall acid gas concentration Chemical equilibrium calculations for all the species present in the liquid phase is needed. More is the amount of available free amine, faster is the rate of reaction between amine and acid gases [4].

Blauwhoff et al. studied MDEA using stirred tank. He found a 2^{nd} order rate constant of $4.8m^3$/kmole/sec at 293K.he reported that it is hard to get a constant absorption rate with MDEA. He assumed 1^{st} order mechanism with respect to MDEA. Critchfield and Rochelle showed results of CO_2 absorption over a range of temperature (282-350K). The nominal pressure for CO_2 was 1 atm [19].

Toman and Rochelle studied the absorption of CO_2 into 50% MDEA and another solution with same strength neutralized with sulfuric acid. The rate constant was to found to be little higher which suggested a weak catalytic effect. Hence, Glasscock proposed a rate expression that showed this decrease as a consequence of depletion of hydroxide ion at the interface [19].

$$r=[CO_2][MDEA]\{K_{H2O}(H_2O) + K_{OH^-}(OH^-)\} + K'_{OH^-}[CO_2][OH^-] \quad \text{-- (2.7)}$$

CHAPTER-3

METHYLDIETHANOLAMINE SYSTEM

3.1 DETAILED DESCRIPTION OF THE PROCESS

The process used for capturing CO_2 using MDEA can be divided into 3 different sections:

1. Cooling of Flue gas and its compression
2. Absorption of CO_2 and solvent regeneration
3. Compression of CO_2

A detailed flowsheet of the process is given below:

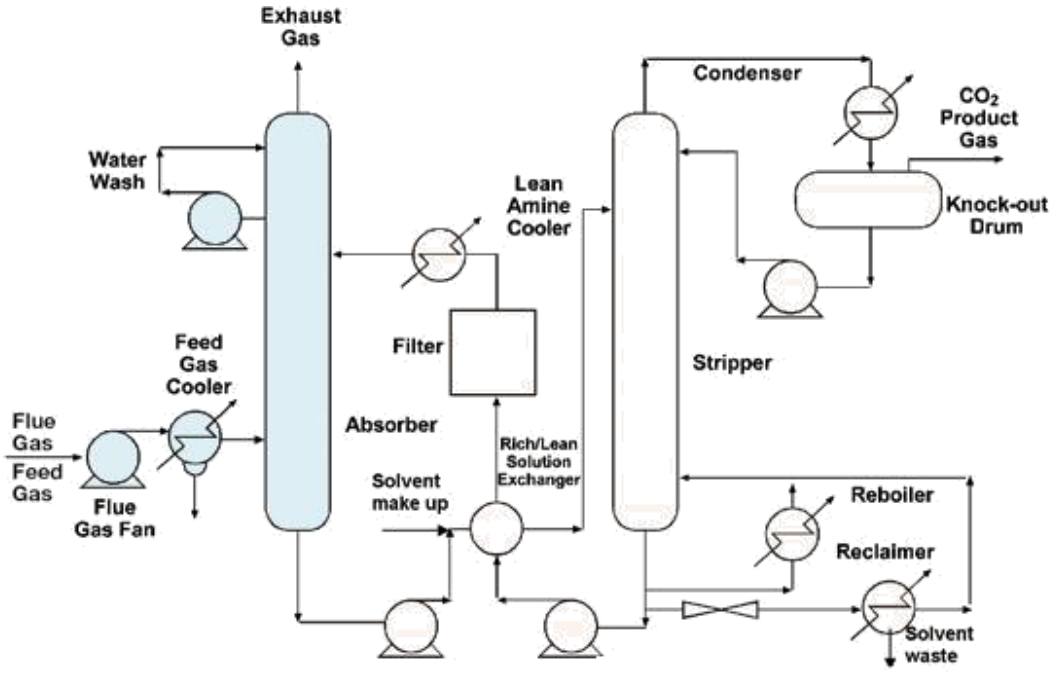

Figure 3-1: Flowsheet for CO_2 capture by MDEA solvent [20]

3.1.1 COOLING OF FLUE GAS AND COMPRESSION

The absorber for the CO_2-H_2O-MDEA system should operate at temperature of around 40°C and therefore, the gases temperature at the inlet of the absorber should lie in the temperature ranging from 40-50°C. Usually, the flue gases temperature at the exhaust in industries ranges from 110-120°C and hence, the flue gases must be cooled before feeding it to the absorber. Sometimes wet flue gas desulfurization scrubber is used for cooling the flue gases. If the flue gases have not been through a scrubber then cooling is done by other means.

Direct contact cooling tower (DCC) is used for cooling the flue gases by feeding it the tower.DCC may be tray tower or packed tower where counter-current flow of flue gases and the cooling water takes place. The flue gas is fed from the bottom of the tower whereas cooling water is fed from the top. Inside the tower, the flue gas is cooled by water evaporation and hence, at the exit the water content of the gas is diminished at the exit of the tower. From the bottom of the tower the cooling water is collected and is sent again to another cooling tower for lowering the temperature so that it can be used gain in the DCC.

The flue gas coming out of the DCC needs to be compressed and therefore, it is sent to a blower. Because of the upward movement of the flue gas in the absorber (tray column), the pressure of the flue gas needs to be raised before feeding to the absorber. Along with the pressure, temperature is also increased. Flue gas needs to be scrubbed prior to chemical absorption with MDEA to remove NO_x, SO_x and other impurities, which react irreversibly with MDEA to form heat stable salts which cannot be reclaimed. The recommended concentration for NO_2 should be less than 20 ppmv [21]. Similarly the recommended concentration for SO_x should be less than 10 ppmv for MDEA solvent [21]. A wet electrostatic precipitator or a mist eliminator must be employed in the flue gas desulfurization unit [21] so as to remove SO_3, which can form sulfuric acid aerosol in scrubbers which can cause corrosion.

3.1.2 CO_2 ABSORPTION AND SOLVENT REGENRATION

The absorber used is a tray column, where vapor and liquid leaving the stage are in equilibrium. From the absorber's bottom, flue gas is fed whereas lean amine solvent is fed from the top. The loading of the lean amine stream which is entering to the absorber from the top is between 0.3-0.35 and rich amine stream leaving the absorber has a loading close to 0.8. In a MDEA system, the loading is defined on a mole basis as given by

$$\text{Loading} = \frac{\text{Moles of } CO_2}{\text{Moles of MDEA}} \qquad \text{-- (3.1)}$$

The amine stream which is stripped off CO_2 is referred to as Lean amine off i.e. the amine stream entering from the absorber's top. If the amine stream has CO_2 loaded in it, then it is known as rich amine i.e. the stream leaving from the absorber's bottom. The lean amine stream is entering inside the absorber through the second stage from the top and make-up water is entering at the top stage.

The rich amine leaving at the absorber's bottom is sent to the heat exchanger, which is also known as cross-heat exchanger, via a pump. In the cross heat-exchanger, the heat is exchanged between the rich amine stream from the absorber and the lean amine stream from the desorber.

As a result, rich stream gets heated up and lean stream gets cooled down. Before the lean amine stream is fed to the absorber, it is again cooled to bring the temperature below 40°C.

The desorber is fed with the rich stream from the cross-heat exchanger. The desorber used here is a tray column which has a reboiler of kettle type. The desorber typically operates at slightly elevated pressure of 1.7-1.8 atm. The rich amine is fed at the second stage of the desorber and flows downward inside the column, opposite to the vapors' direction from the reboiler. The stream that is coming out from the top of the desorber is sent to a condenser where water is condensed and the temperature is lowered and then sent to a flash to separate the CO_2 from H_2O [22].

3.1.3 SOLVENT RECLAIMATION

A MDEA reclaimer is used necessarily when the flue gas is coming out from coal fired power plants to treat the stable salts that are formed because of SO_x and NO_x. These salts should not accumulate on the amine stream as it is not desirable since it reduces the solvent's capacity for absorbing CO_2. The removal of the purge stream of MDEA solvent is done and is then sent to the reclaimer where strong alkali like NaOH and heat are added because of which heat stable salts can be dissociated contributing to the recovery of the solvent [22].

3.1.4 CO_2 COMPRESSION

The CO_2 gas coming out from the desorber's top needs to be dried and should be compressed before sending it for storage. Drying is one of the important steps as the presence of even small amount moisture in the stream can corrode the pipelines, which are used for transporting CO_2. Typically, a reciprocating compressor with 4 stages is used for cooling. The compressor is employed for compressing the CO_2 to a pressure of 90 atm, after which the liquid CO_2 can be pumped through pump with the discharge pressure of 130 atm [22].

3.2 MODELLING USED

Types of modeling used

1. Thermodynamics modeling

2. Rate based modeling

3.2.1 THERMODYNAMIC MODEL

The thermodynamic model was described along with the help of electrolyte-NRTL frame work. A model for the Absorption/Stripping process demands the use of rigorous thermodynamics. Even though CO_2 absorption is a non-linear process, information about the equilibrium composition of the CO_2-MDEA-H_2O system is required for determining driving forces in liquid phase and solution speciation [23].

3.2.1.1 SOLUTION CHEMISTRY AND EQULIBRIUM GOVERNING EQUATIONS

The following reversible reactions occur in the liquid phase when CO_2 is absorbed into an aqueous solution of MDEA [24]

$$R_3NH^+ = R_3N + H^+ \quad \text{-- (3.2)}$$

$$CO_2 + H_2O = H^+ + HCO_3^- \quad \text{-- (3.3)}$$

$$HCO_3^- = H^+ + CO_3^{2-} \quad \text{-- (3.4)}$$

$$H_2O = H^+ + OH^- \quad \text{-- (3.5)}$$

Corresponding expressions of equilibrium rate constants are:

$$K_1 = (a_{R3N}\, a_{H+})/(a_{R3NH}) \quad \text{-- (3.6)}$$

$$K_2 = (a_{H+}\, a_{HCO3}^-)/(a_{CO2}\, a_w) \quad \text{-- (3.7)}$$

$$K_3 = (a_{H+}\, a_{CO3}^{2-})/(a_{HCO3}^-) \quad \text{-- (3.8)}$$

$$K_4 = (a_{H+}\, a_{OH-})/(a_w) \quad \text{-- (3.9)}$$

The equilibrium constants of the above mentioned reactions are calculated from the reference-state participating components' Gibbs free energies:

$$-RT \ln K_j = \Delta G_j(T) \quad \text{-- (3.10)}$$

Where Kj denotes the equilibrium constant for the reaction j, $\Delta Gj°(T)$ denotes the Gibbs free energy change for reaction j reference-state at temperature T, R denotes the universal gas constant, and T denotes the temperature of the system [25].

For the aqueous phase reactions, the reference states chosen for the solvents (water and MDEA) are pure liquid, and for the solutes at infinite dilution. The calculation of the solvents' Gibbs free energy is done by the function shown below:

$$G_s(T) = G_s^{ig}(T) + \Delta G_s^{igfl}(T) \quad \text{-- (3.11)}$$

where $G_s(T)$ denotes the solvent *s* Gibbs free energy at temperature T, $G_s^{ig}(T)$ denotes the solvent s ideal gas Gibbs free energy at temperature T, and $\Delta G_s^{igfl}(T)$ denotes the departure of Gibbs free energy from ideal gas to liquid at temperature T.
The calculation of the Gibbs free energy for an ideal gas is done from the Gibbs free energy of formation for an ideal gas at 298 K, the enthalpy of formation for an ideal gas at 298 K, and heat capacity for the ideal gas [25].

The heat of absorption for CO_2 in aqueous MDEA solutions can be done from the enthalpy balance for the absorption process:

$$\Delta H_{abs} = \frac{n_{final}H^{l}_{final} - n_{initial}H^{l}_{initial} - n_{CO2}H^{g}_{CO2}}{n_{CO2}} \quad \text{-- (3.12)}$$

where ΔH_{abs} denotes the heat of absorption/mole of CO_2, H^{l}_{final} denotes the final solution's molar enthalpy, $H^{l}_{initial}$ denotes the initial solution's molar enthalpy, H^{g}_{CO2} denotes the gaseous CO_2 absorbed molar enthalpy, n_{final} denotes the total number of moles in the final solution, $n_{initial}$ denotes the total number of moles in the initial solution, and n_{CO2} denotes the number of moles of CO_2 absorbed [25].

There are basically two types of heat of absorption which are 1) integral and 2) differential heat of absorption. The integral heat of absorption for the amine-H_2O-CO_2 system is the heat effect/mole of CO_2 during the CO_2 loading of the amine increasing from 0 to the final CO_2 loading value of the amine-H_2O-CO_2 system. The differential heat of absorption for the amine-H_2O-CO_2 system is the heat effect/mole of CO_2 if meager amount of CO_2 is added to this amine-H_2O-CO_2 system.

For calculating both the types of heat of absorption, enthalpy calculations for the initial and final amine-H_2O-CO_2 systems and for gaseous CO_2 are needed. The calculation for heat capacity of the MDEA-H_2O-CO_2 system can be done from the temperature derivative of enthalpy [25]

The following balance equations for the reacting species can be formed [24]:
Amine balance:

$$M_A = (m_{R3N} + m_{R3NH^+}) \quad \text{-- (3.13)}$$

Carbon balance:

$$M_A y = (m_{CO2} + m_{HCO3^-} + m_{CO3^{2-}}) \quad \text{-- (3.14)}$$

Electroneutrality:

$$m_{R3NH^+} + m_{H^+} = m_{OH^-} + m_{HCO3^-} + 2m_{CO3^{2-}} \quad \text{-- (3.15)}$$

3.2.1.2 ELECTROLYTE-NRTL MODEL

The thermodynamic model developed in this work uses the electrolyte-NRTL theory which was first developed by Chen and Evans in the year 1979 [26, 27] and extended by Mock et al [28, 29] in the year 1986 for mixed solvent electrolyte systems.

The E-NRTL model is a used to determine the excess Gibbs free energy for a solution. It is found that the activity coefficients of every component of mixture can be related to the excess Gibbs free energy by equation [23]

$$Ln¥_i=d/dn_i(G^E/RT)_{T,P,n}\ j\neq I \qquad \text{-- (3.16)}$$

¥ is the activity coefficient of species i in solution, n_i is the number of moles of i, G^E is the excess Gibbs free energy, defined as

$$G^E=G-G^{id} \qquad \text{-- (3.17)}$$

Where G^{id} is the excess Gibbs free energy if the mixture were ideal.The excess Gibbs free energy is related to excess enthalpy and excess entropy of mixing by

$$G^E=H^E-TS^E \qquad \text{-- (3.18)}$$

The excess enthalpy is found from the fact that a species changes its interactions with the surrounding species when the composition is changed. When ions are present in larger amounts in the solution, the interaction with each other is strong and every molecule of CO_2 among them diminishes the intensity of the interaction. It tends to leave the liquid phase when the solution has high ionic strength because this reduces the total enthalpy of the solution. The excess entropy is due to the change in the randomness of the reciprocal position of molecules in the solution. The electrolyte-NRTL model assumed the non ideal entropy of mixing is very less as compared to heat of mixing. It gives an analytical expression for the excess Gibbs free energy. In the model G^E is a sum of three terms, the long range ionic forces, the short range molecular forces and the Born correction [24].

$$G^E=G^{E,\ PDH}+G^{E,\ BORN}+G^{E,\ NRTL} \qquad \text{-- (3.19)}$$

The long term ionic is described with the theory of Debye-Huckel, modified by Pitzer and it depends on ionic strength of the solution. The term $G^{E,\ PDH}+G^{E,\ BORN}$ represents the long range forces contribution with reference state of ions at infinite dilution in water.

The short range force needs to be included for accounting the hydrogen bonds as well as local interactions of molecules with molecules, molecules within parts and ion pairs with ion pairs [24].

3.2.2 RATE MODEL

The modeling of absorption and desorption column is done by the use of thermodynamic models. In the thermodynamic models, the column is defined with specific number of stages and it is assumed that the liquid and vapor leaving each stage are in equilibrium [30]. Though, this is an important assumption, it may not be valid in real case scenario. However to make it applicable for real case scenarios, factors like the height equivalent to a theoretical plate (HETP), Murphee and stage efficiencies are used [31]. Even after the above factors are used, it does not work properly as there are large deviations from the equilibrium model [32] .Therefore, t is necessary to use the rate-based models.

The modeling of absorption and desorption columns by rate-based model is done by the rate-based mode of RADFrac, ASPEN RateSep. In this type of modeling chemical reactions kinetics as well as heat and mass transfer phenomena are included [33]. By the help of Aspen RateSep, various equations are solved, which are:

- Balance equation for Heat and mass both for the liquid and vapor phases.
- Rate models for Heat and mass transfer to determine the transfer rates at the interphase.
- Equations for Vapor-liquid equilibrium at the interphase.
- Estimation of coefficients for heat and mass transfer as well as interfacial areas.
- Improvement of heat and mass transfer processes through chemical reactions.

CHAPTER-4

SIMULATION BY THERMODYNAMIC MODELLING

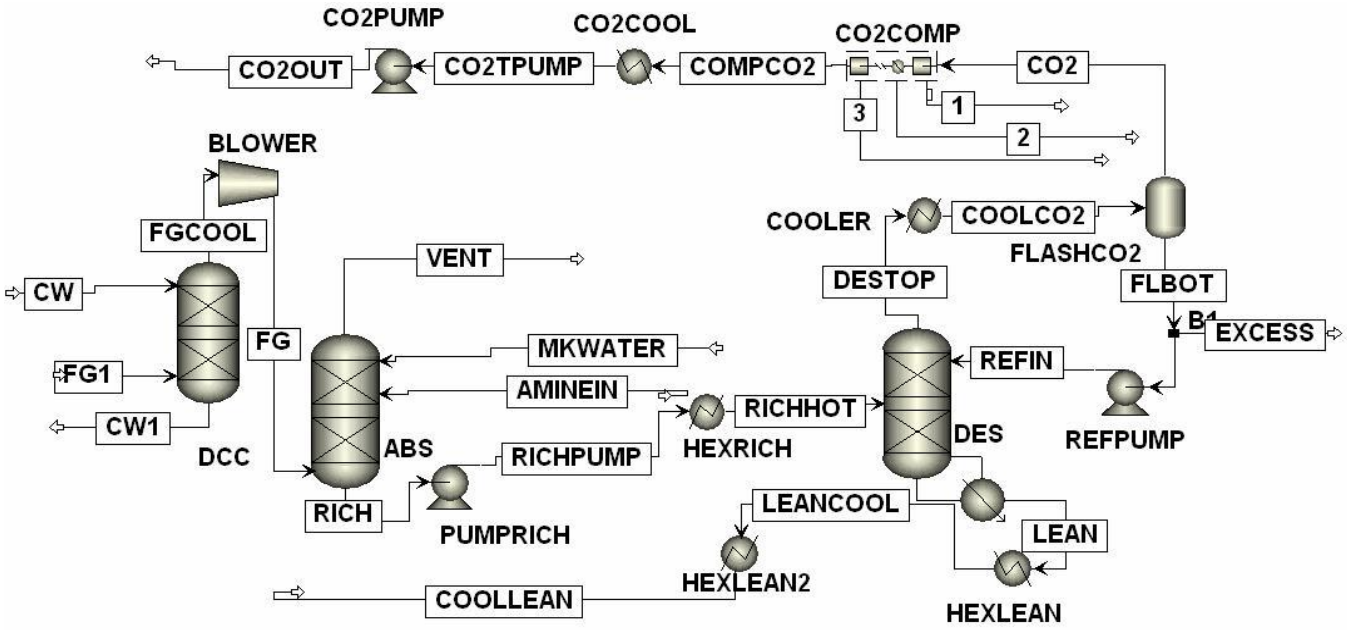

Figure 4-1: Process flow diagram of MDEA system as developed in ASPEN Plus[35]

Since the main reason for this type of modeling was to study the vapor-liquid equilibrium of system, the open-loop simulation was modeled for easier convergence and multiple runs can be done quickly. In order to make the simulation converged in the closed form, the various types of design specifications were used.

In the thermodynamic model, the absorber and desorber column used are designed with specific number of stages, where each stage is in equilibrium. In the column, the reactions taking place are also assumed to be in equilibrium. Thus, the most optimistic results are obtained from this simulation. In real case scenarios, the reactions are not in equilibrium and mass and heat transfer considerations inside the column would invalidate the thermodynamic modeling. The main reason for these simulations is for obtaining a lower limit upon the heat duty and good estimations were provided for converging the system with the complex rate-based model.

The flow sheet shown above is developed by using ASPEN Plus software. The RADFrac columns were selected for modeling the absorber, desorber and direct contact cooling tower (DCC). The desorber used here has a reboiler of kettle type. A high pressure separator, known as flash is used for separating the CO_2 from water. A dot splitter was used to remove the excess

water and a fraction was recycled back to the desorber. The CO_2 so obtained was sent to the reciprocating compressor with 4 stages where cooling is done between stages. In each stage a gradual compression takes place and finally CO_2 was obtained at a pressure of 90 atm. The compressor was a MCOMP model and water was decanted out in each stage. A set of pumps and heaters were selected and used for varying pressure and temperature to the required value.

4.1 PROCEDURE FOR DEVELOPING THE FLOWSHEET

1) After providing the project title and name of the account, first the different components were selected as shown below.

Figure 4-2: Different components selected in ASPEN PLUS

2) After selecting the components we set the base method as E-NRTL and all the properties were defined according to it.

3) The different input streams were next given. The Flue gas was initially fed to the DCC at a temperature and pressure of 115^{o}C and 1 atm respectively along with cooling water at 25^{o}C and pressure of 1 atm. MDEA was then fed at 40^{o}C with a pressure of 2 atm and with a flow rate of 65 kg/hr with initial CO_2 loading of 0.3 to the absorber for absorption. Make up water was provided to the absorber at temperature of around 35^{o}C and 2 atm pressure to prevent entrainment amine stream.

4) After the streams were successful specified, next the input for different blocks were provided. The input specification for the different pumps and heaters are given below:-

Table 4-1: Input specification of pumps

PUMPS	DISCHARGE PRESSURE(atm)
PUMPRICH	3
REFPUMP	3.5
CO2PUMP	130

Table 4-2: Input specification of heaters

HEATERS	TEMPERATURE(℃)	PRESSURE(atm)
HEXRICH	50	3
HEXLEAN	50	1.1
HEXLEAN2	40	1
COOLER	30	1.5
CO2COOL	35	100

5) For the DCC, number stages were fixed at 4 with no condenser and the stage1 pressure was set at 0.9 atm .A reflux ratio of 2 was maintained for the column. For the Absorber, the number of stages was fixed at 12 with no condenser or reboiler and the stage1 pressure being 1.5 atm. In the case of the Desorber, 8 stages were taken with a kettle reboiler and the stage1 pressure was set at 1.8 atm. Reboiler duty was taken as 5655KJ/Kg. For the desorber a pumparound was defined. It represented an internal reflux from a hotter stage to a cooler one. In this case the pumparound was given from 8^{th} stage to the 1^{st} stage.

6) A blower was also used to raise the pressure of the cooled flue gas. It was modeled as an isentropic blower with discharge pressure of 2 atm.

7) A 4 stage reciprocating compressor was selected and modeled as isentropic one. The outlet stream was obtained at 90atm and 50^{o}C. From all the other stages water was purged out.

8) The required reactions mentioned earlier were given and the temperature dependent constants were provided according to the table given below:-

Table 4-3: Reaction data used for the reactions [35]

REACTION	A	B	C	D
2.2	132.89	-13445.9	-22.47	0
2.3	231.46	-12092.1	-36.78	0
2.4	216.05	-12431.7	-35.48	0
2.5	24.76	-8989	0	0

9) After providing all the input information the different design specification were given for optimizing and converging the simulations.

The design specifications used in the flowsheet are given below [35]:

1. **Vent CO_2:** The amount of CO_2 that is coming out from the top of the absorber is regulated by a design specification and the desired extent of capture can be achieved by varying the amine flow rate to the absorber. The above design specification can be specified by selecting the *Flowsheeting Options* tab.

   For this, first the mass flow rate of AMINEIN and VENT stream were defined. The mass flow rate of the VENT stream was desired to be 1.2 kg/hr assuming 90 % absorption takes place in the absorber with a tolerance of 0.05. The AMINEIN flow rate was varied from 50-70 kg/hr to achieve this target.

2. **Reboiler Duty:** The reboiler duty provides the necessary heat required to produce steam which carries the CO_2 upwards from the rich amine and helps in stripping .Since the flowsheet is an open loop one, we need to match the composition of the stream coming out of the second heat exchanger after desorber, COOLLEAN with AMINEIN stream for ensuring the convergence of the simulation in closed loop manner. This is achieved by matching the loadings of the two streams. For matching the loading we need to first define two property sets FAPPCO2 and FAPPMDEA in Prop sets tab under the Property option. These property sets are used for calculating the apparent molar flow rate of CO_2 and MDEA in the stream. The ratio of FAPPCO2 to FAPPMDEA is the loading of the stream. The property was set to the desired value (the value in the AMINEIN stream) and the reboiler duty was varied until the desired value is achieved.

   After the prop sets have been defined, design specification of the desorber was specified. This design specification checks the property ratio or the ratio of the two prop sets of the LEAN stream coming out of the desorber. The reboiler duty was varied from 3000 to 6000 KJ/Kg to reach the desired loading of 0.3 as of the AMINEIN stream.

3. **Cross-exchanger heat duty:** In the flowsheet shown above, the two separate heat

exchangers – HEXRICH and HEXLEAN function together as a cross heat exchanger for ensuring that the closed loop is not formed. However, the heat duties of both the heat exchangers are matched so that they can effectively function as the cross-heat exchanger. This was achieved by using the above design specification in the *Flowsheeting Options* tab. The heat duty of the HEXLEAN was set equal to the negative of the heat duty of the HEXRICH.

Initially the heat duties of the two heat exchangers were defined. Since we have assumed that the heat duties of HEXRICH and HEXLEAN are equal but of opposite sign it was specified that the sum of the heat duties is desired to be 0 with a tolerance of 0.02. The mass flow rate of AMINEIN stream was varied from 50-70 kg/hr to satisfy the desired condition.

4. **Cross-heat exchanger approach temperature:** Along with matching the heat duties of heat exchangers HEXLEAN and HEXRICH, it was necessary to specify a design specification on the temperature approach of the cross-exchanger. For this purpose, the temperature of the inlet stream of HEXRICH is set to 10°C below the temperature of the outlet stream of HEXLEAN.

   For this purpose first the temperature of LEANCOOL and RICHPUMP were defined. It was specified that the temperature of LEANCOOL to be 10^{o}C more than the temperature of RICHPUMP with a tolerance of 0.1. To achieve this we need to vary the AMINEIN mass flow rate from 50-70 kg/hr.

5. **Water balance:** Water balance in the plant has to be maintained in order to have convergence in closed loop manner. Therefore, the flow rate of the MKWATER stream was varied to achieve the overall water balance.

To ensure water balance we first need to define the mass flow rate of CW, CW1, MKWATER, 1, 2 and 3 stream was defined. It was specified that sum of the expression (CW+MKWATER-CW1-1-2-3) should be equal to zero with a tolerance of 0.02.To attain water balance we need to vary the MKWATER from 40-60 kg/hr.

CHAPTER-5

RESULTS AND DISCUSSION

After the initial run we found the CO_2 conversion to be 75 %.Next we need to carry out sensitivity analysis for the complete process to see the effect of different parameters on loading and energy required in the form of Reboiler Duty. The results of this analysis are stated below:-

5.1 VARIATION OF L/G IN ABSORBER WITH LEAN LOADING FOR 80 % CAPTURE

Table 5-1: Lean loading vs L/G data

Lean loading(mole of CO_2/mole of MDEA)	L/G (total molar flow of liquid/total molar flow gas)
0.08	0.7
0.12	0.8
0.14	0.85
0.16	0.87
0.18	0.9
0.2	0.95
0.22	1
0.24	1.1
0.26	1.2
0.28	1.4
0.30	1.5

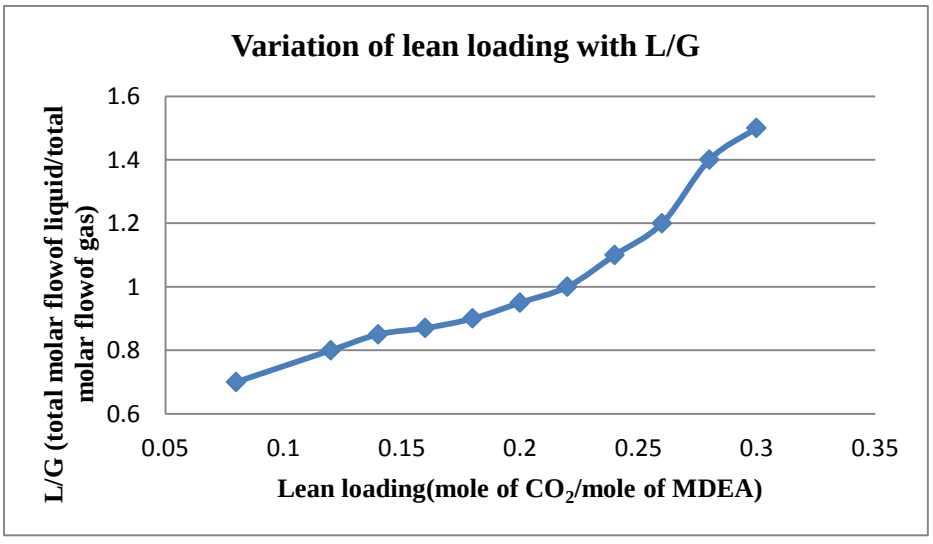

Figure 5-1: Variation of L/G with lean loading for 80% CO2 capture

DISCUSSION

It was observed from the above figure that with the increase in loading of the lean amine stream, the flow rate of the amine increases. It is due to the reason that the loading is directly proportional to its capability to absorb CO_2 and with increase in loading the capacity to absorb CO_2 increases. It was also found that there is a sharp increase in the L/G or Amine flow rate required to achieve the required amount of capture after a certain loading.

5.2 VARIATION OF REBOILER DUTY WITH L/G IN ABSORBER FOR 80 % CAPTURE

Table 5-2: Data representing variation of reboiler duty with L/G in absorber

L/G(total molar flow of liquid/total molar flow of gas)	Reboiler duty(kJ/kg)
0.75	5500
0.78	5000
0.8	4800
0.85	4400
0.9	3560
0.95	3580
1.05	3600
1.1	3615
1.2	3630
1.4	3640
1.45	3645

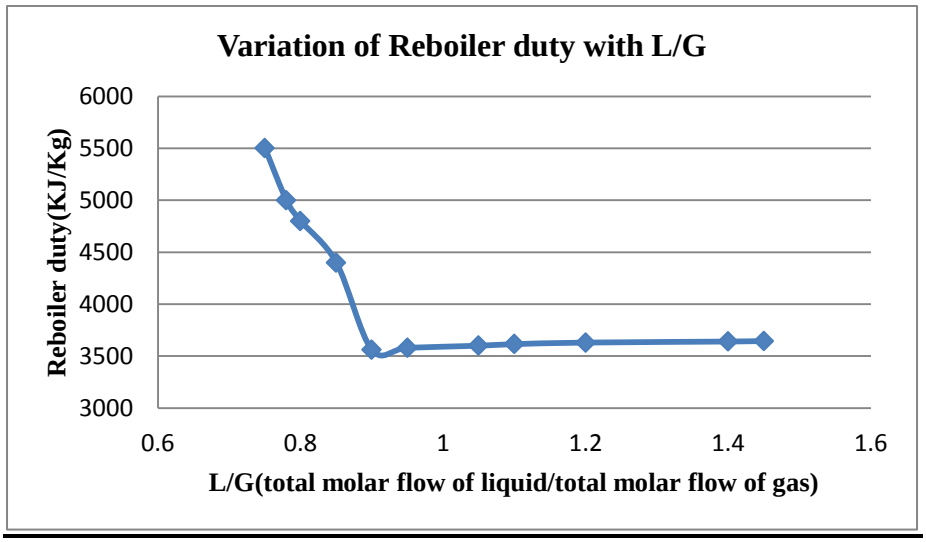

Figure 5-2: Variation of reboiler duty with L/G for 80% CO2 capture

DISCUSSION

It can be seen from the figure mentioned above that the reboiler duty is both directly and indirectly proportional to Lean loading. Reboiler Duty was high at lower lean loadings, as the equilibrium partial pressure of CO_2 is very low at low loading. Therefore, for stripping the solution to the desired lean loading in the desorber, large amount of steam is needed. Thus, energy lost because of water condensation as well as vaporisation is high. Though, the amount of steam that is required for vaporization decreases as the equilibrium partial pressure of CO_2 increases as the lean loading increases. This results in lowering of reboiler duty. However, after certain lean loading, the sensible heat component dominates as the flow rate of the liquid for achieving 80% capture is increased as shown in Figure 5-2. Thus, scope for optimization of the loading range exists to operate in.

5.3 EFFECT OF CAPTURE PERCENTAGE

Table 5-3: Variation of reboiler duty with lean loading at different capture percentage

Lean loading(mole of CO_2/mole of MDEA)	Reboiler duty at 65% CO_2 capture	Reboiler duty at 85% CO_2 capture	Reboiler duty at 90% CO_2 capture
0.08	5680	5700	5730
0.12	4779	4800	4820
0.14	4380	4400	4425
0.16	4130	4150	4180
0.18	3530	3560	3600
0.2	3560	3580	3615
0.22	3570	3590	3620
0.24	3585	3615	3650
0.26	3595	3630	3670
0.28	3610	3640	3785
0.3	3620	3650	3820

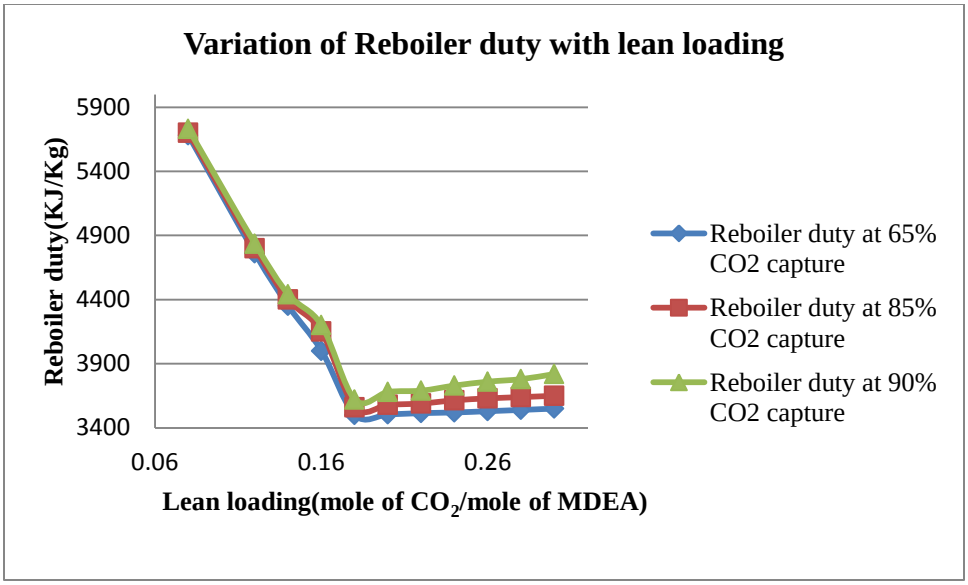

Fig 5-3: Variation of reboiler Duty with lean loading for different capture percentage

DISCUSSION

The above figure tells us about how the capture% affects the reboiler duty. Capture extents for 65%, 85% and 90% are studied. The reboiler duty for different loadings at various capture percentage was calculated. It was found out from the figure that the reboiler duty/kg of CO_2 captured increases with the capture % . This may be due to the fact that with the increase in the required solvent flowrate, the capture percentage increases and as a result sensible heat required for the system also increases.

5.4 VARIATION IN REBOILER DUTY WITH DESORBER TEMPERATURE AND DESORBER PRESSURE FOR 80 % CO_2 CAPTURE

Table 5-4: Data representing variation of reboiler duty with temperature and pressure of the desorber for 80% capture

Desorber pressure(kPa)	Reboiler Duty(KJ/Kg)	Desorber Temperature(K)
75	5700	370
100	4800	378
125	4400	383
150	4150	387
175	3800	391
200	3750	394
225	3720	396
250	3700	399
275	3660	402
300	3620	405

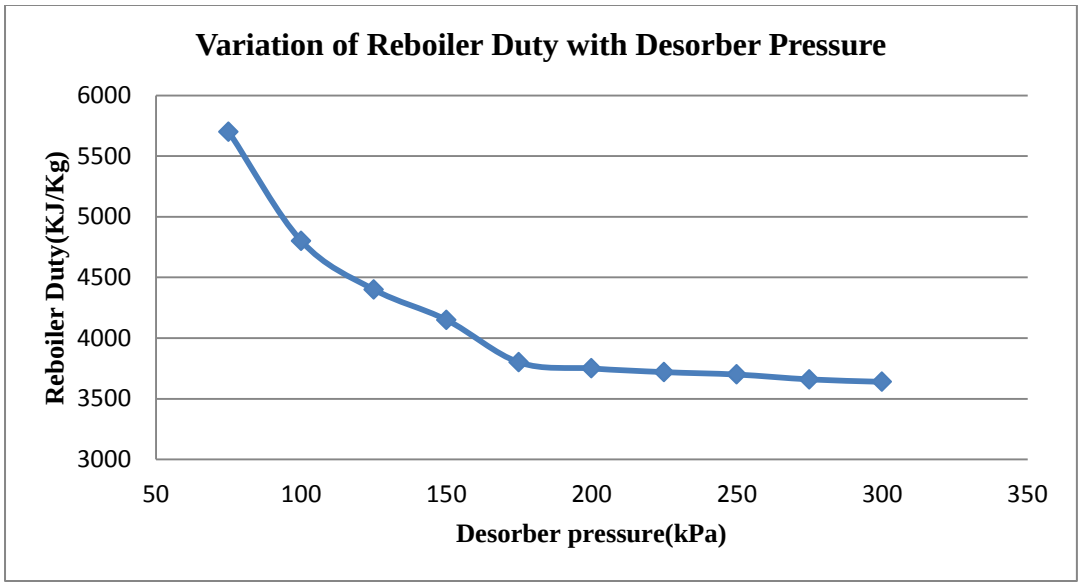

Fig 5-4: Graph showing variation of reboiler duty with desorber pressure

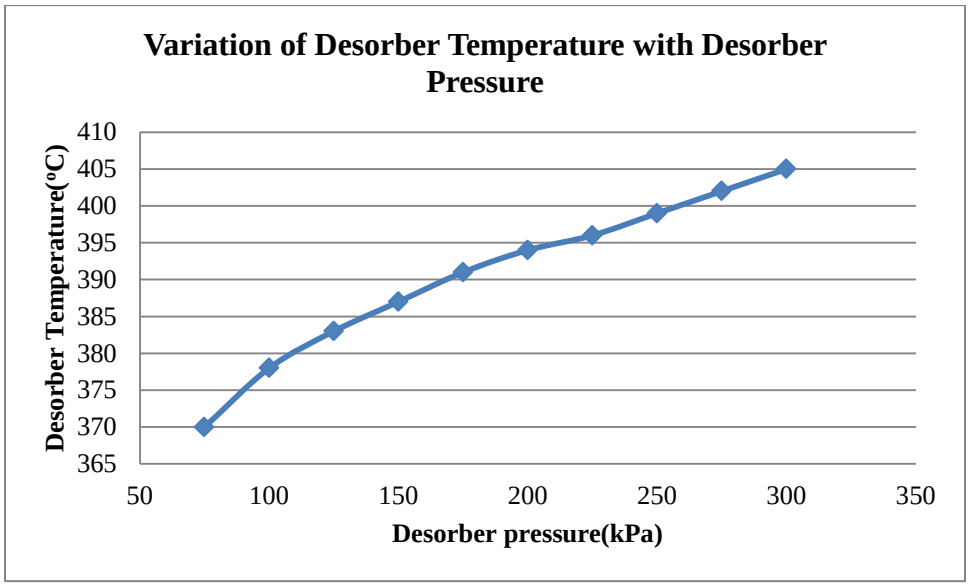

Fig 5-5: Graph showing variation of desorber temperature with desorber pressure

DISCUSSION

The process performance is very sensitive to desorber temperature and pressure.The pressure is directly related to temperature. With the increase in temperature pressure also increases. As at high temperature and pressure transfer of CO_2 takes place, it is desired to maintain the desorber at high temperatures and pressures. However, it should be kept in mind that with increase in

temperature degradation of solvent (MDEA) takes place. Therefore, it is recommended to maintain the desorber within the temperatrure of 130°C.

5.5 VARIATION IN REBOILER DUTY WITH LEAN LOADING FOR APPROACH TEMPERATURES OF 5 &10 ^{O}C

Table 5-5: Data representing variation of reboiler duty with lean loading for different temperature approach

Lean Loading(mol of CO_2/mole of MDEA)	Reboiler Duty For 10 ^{O}C Cross Heat Approach(KJ/Kg)	Reboiler Duty For 5 ^{O}C Cross Heat Approach(KJ/Kg)
0.08	5700	5700
0.12	4800	4800
0.14	4400	4400
0.16	4150	4150
0.18	3560	3500
0.2	3580	3480
0.22	3590	3450
0.24	3615	3470
0.26	3630	3490
0.28	3640	3510
0.3	3650	3530

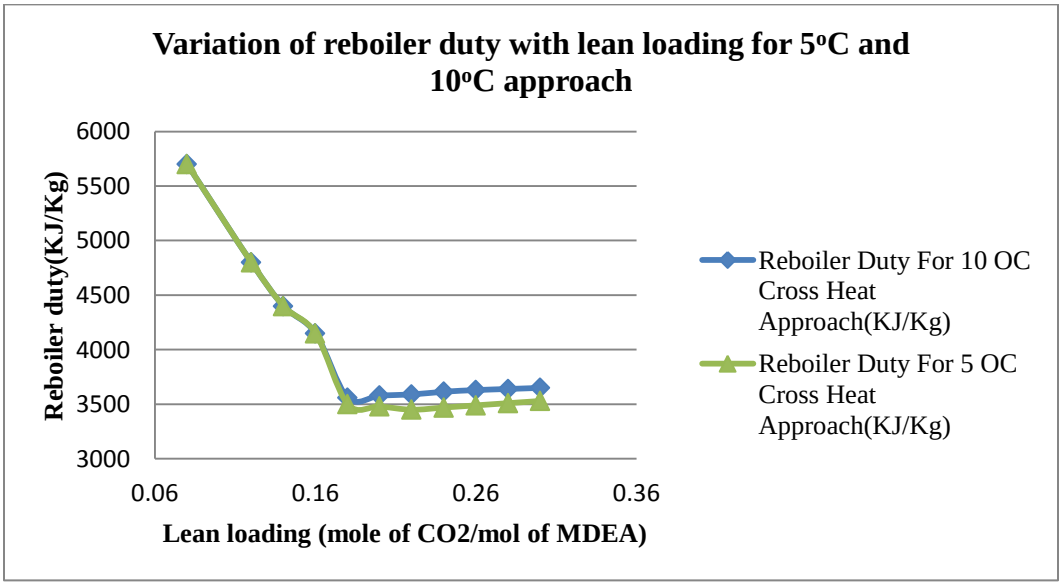

Fig 5-6: Graph showing variation of reboiler duty with cross-heat exchanger approach

DISCUSSION

The effectiveness of cross-heat exchangers was found out from temperature approach. Generally the cold side approach is more than hot side. From the above figure it was found that Reboiler duty is less for 5 ^{O}C approach as compared to 10 ^{O}C approach. Reboiler duty at higher lean loadings for 5 ^{O}C is almost constant. We are not getting variation in reboiler duty. It is not that much effective. Therefore, 10 ^{O}C approach is used.

CHAPTER-6

6.1 CONCLUSION

To carry out simulation and modeling for the CO_2 capture process with MDEA, the E-NRTL model was used to correlate vapor-liquid equilibrium properties of CO_2-H_2O-MDEA system with the experimental data available for the CO_2-H_2O-MDEA system. The model is validated to predict vapor-liquid equilibrium (VLE), Reboiler duty, and partial pressure of CO_2 of the MDEA-H_2O-CO_2 system with temperature ranging from 40^OC to 120^OC, concentration of MDEA up to 30wt %, and loadings of CO_2 close to 1. The model provides a representation for thermodynamic property for the CO_2- H_2O-MDEA system over a wider range of conditions and gives more-reliable predictions than those from previous works.

The models were confirmed to be able to represent thermodynamic and thermal properties over a broad range of conditions. Overall the results presented above indicate that the developed model, through simultaneous regression to different kind of data, gave a set of optimum parameters for CO_2-MDEA-H_2O.The developed models adequately represent thermodynamic and thermal properties of the systems. Modeling results show that the developed models improved significantly over previously existing models. The relation of CO_2 capture on the lean loading, desorber temperature and pressure, and reboiler duty, was sufficient to ensure the completion of the simulation and designing of the Carbon Capture and Storage project work.

The system was well represented by the E-NRTL model. However, because of high complexity of model equations, the implementation becomes difficult.

6.2 FUTURE SCOPE OF WORK

A recurring theme in this work is that there are no rules of thumb which always apply; every situation is different. Many rules of thumb are presented in the literature and most of them are based on established criterion and work. However, just because they work in most situations does not mean they are always the best choice. This work should be considered as a starting point, a first guess. A thorough evaluation should be performed to optimize performance. The benefits of deviating from these guidelines should be weighed against the risks.

As the rate of reaction of CO_2 with MDEA is low, the thermodynamic model should be further developed for aqueous MDEA blended with PZ or other additives like Sulfolane.

Accurate simulation can provide increased ability to anticipate the effect of changing treating conditions in the plant.The future work should emphasize on high percent removal of the gas for optimum conditions.

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